

PTO 08-1028

CC = JP  
19880405  
Kokai  
63075009

METHOD FOR CONTINUOUS PRODUCTION OF POLYETHYLENE  
BY MULTI-STAGE POLYMERIZATION  
[Tadan jugo ni yoru poriechiren no renzoku seizo ho]

Kansei Chiba

UNITED STATES PATENT AND TRADEMARK OFFICE  
WASHINGTON, D.C. DECEMBER 2007  
TRANSLATED BY: THE MCELROY TRANSLATION COMPANY

PUBLICATION COUNTRY	(19):	JP
DOCUMENT NUMBER	(11):	63075009
DOCUMENT KIND	(12):	Kokai
PUBLICATION DATE	(43):	19880405
APPLICATION NUMBER	(21):	61220033
APPLICATION DATE	(22):	19860918
INTERNATIONAL CLASSIFICATION <sup>4</sup>	(51):	C 08 F 10/02 2/00 4/64
INVENTOR	(72):	Kansei Chiba
APPLICANT	(71):	Chisso K.K.
TITLE	(54):	METHOD FOR CONTINUOUS PRODUCTION OF POLYETHYLENE BY MULTI-STAGE POLYMERIZATION
FOREIGN TITLE	[54A]:	Tadan jugo ni yoru poriechiren no renzoku seizo ho

## Claims

1. A method for producing polyethylene by continuous, multi-stage polymerization wherein a low molecular weight polymer is produced in a first stage of polymerization and a high molecular weight polymer is produced in a second stage of polymerization from ethylene with a Ziegler-type catalyst in the presence of a solvent and hydrogen using multiple polymerization reactors in series, and said method for producing polyethylene by continuous, multi-stage polymerization is characterized in that a glycol compound is added continuously to the polymerization mixture, which is extracted from said first polymerization stage before entering the second polymerization stage, at 0.1-10 mol/atom versus the transition metal atom carried by the catalyst in said mixture.

2. The method for continuous production of polyethylene described in Claim 1, wherein a small quantity of  $\alpha$ -olefin (excluding ethylene) is fed to the first stage and/or the second stage of polymerization for copolymerization with ethylene.

3. The method for continuous production of polyethylene described in Claim 1, wherein one tank or a series of 2 tanks and a catalytic system consisting of titanium-supporting solid catalytic substance (I) and an organic aluminum compound (II) are utilized in the first stage of polymerization.

4. The method for continuous production of polyethylene described in Claim 3, wherein the reaction product produced by reacting solid product (IV), obtained by reacting a trivalent metal halide with a divalent metal hydroxide, oxide, carbonate, complex salts thereof or divalent metal compound hydrate, with polysiloxane (V) and tetravalent titanium compound (VI) is utilized as the titanium-supporting solid catalytic substance (I).

5. The method for continuous production of polyethylene described in Claim 1, wherein

(i) the first stage of polymerization is conducted in a saturated hydrocarbon solvent at a polymerization temperature of 50-120°C and polymerization pressure of 2-70 kg/cm<sup>2</sup> under the

condition of having a gas phase in the upper reactor by feeding 30-80 wt% of the total quantity of ethylene and hydrogen to maintain an ethylene to hydrogen molar ratio of 1/3.0 to 1/7.0 in the gas phase in the polymerization reactor; /2\*

(ii) the second stage of polymerization is conducted by drawing the polymer suspended in the solvent to a pressure of 1-60 kg/cm<sup>2</sup> after completing the first stage of polymerization and recycling at least part of the hydrogen in the gas phase back to the first stage of polymerization, followed by polymerizing at a polymerization temperature of 30-100°C and polymerization pressure of 2-70 kg/cm<sup>2</sup> under the condition of having a gas phase for said suspended polymer product by feeding 10-70 wt% of the total quantity of ethylene and hydrogen to maintain an ethylene to hydrogen molar ratio of 1/0.001 to 1/0.1 in the gas phase in the polymerization reactor.

#### Detailed description of the invention

##### Technical field

This invention pertains to a method for continuous production of polyethylene by multiple-stage polymerization. More particularly, it pertains to said method for continuous production of low molecular weight polymer in a first stage of polymerization and high molecular weight polymer in a second stage of polymerization.

The polyethylene obtained by the method of the present invention is suitable for hollow molding or extrusion molding and can produce finished products with excellent physical properties and extremely low formation of fish eyes (F.E.)

---

\* [Numbers in right margin indicate pagination of the original text.]

Prior art

High molecular weight (low melt index) polyethylene with proper strength and easy processing is required for extrusion molding products or hollow molding products, the main applications for polyethylene. Low melt index polyethylene has excellent strength but also has the drawback of poor flow property during molding. Measures for solving this problem include the method of widening the molecular weight distribution of the polymer. Polyethylene with a narrow molecular weight distribution is suitable for injection molding, but polyethylene with a broad molecular weight distribution is more desirable for extrusion molding or hollow molding.

When polyethylene with a narrow molecular weight is subjected to hollow molding, the extrusion pressure tends to increase excessively during molding; the molding becomes difficult or significant defects occur in the product appearance due to formation of strands or pits or melt fracture. In the case of extrusion molding, fatal or undesirable influence from excessive extrusion pressure or increasing instability during molding can significantly reduce the product value. To solve such problems, the molecular weight distribution is widened to improve the processing property and productivity and produce products with excellent appearance.

Methods for expanding the molecular weight distribution include incorporating a third ingredient in the polymerization system, utilizing a mixture of 2 types of organic aluminum compound serving as one of the catalysts and utilizing a catalyst having many polymerizing active centers. However, producing the polymers with sufficiently broad molecular distribution is hardly an easy task. In this regard, methods by multi-stage polymerization are known as measures for significantly broadening the molecular weight distribution and for regulating it at will as well, but said methods are not necessarily satisfactory. For example, Japanese Kokai Patent Application No. Sho 51[1976]-47078 disclosed a continuous, multi-stage polymerization method for producing low molecular weight polymer in a first

stage of polymerization and high molecular weight polymer in a second stage of polymerization using a combination of a supported catalyst substance and an organic metal compound. The drawbacks of said method are that a high polymerization temperature of 120-250°C is required for the solution polymerization and a substantially large quantity of solvent is utilized for dissolving the polymer.

Japanese Kokai Patent Application No. Sho 48[1973]-42716 disclosed a method wherein the polymerization system was opened up after completing the first stage of polymerization to release the gas from the gas phase, followed by resetting the polymerization conditions to conduct the second stage of polymerization. However, such batch processing significantly reduces the productivity of the polymerization.

Also, Japanese Kokai Patent Application No. Sho 57[1982]-128707 and No. Sho 60[1985]-177008 and others disclosed many methods of conducting 2-stage, continuous polymerization of ethylene using specific catalysts by specifying the mixing ratio and the difference in molecular weight for the polymers of the 1<sup>st</sup> and the 2<sup>nd</sup> stage of polymerization. However, the larger the difference in the molecular weight distribution is between the first stage and the second stage when conducting these methods, the more significant is the formation of fish eyes (F.E. hereafter) in the final products. Accordingly, simultaneously solving the problems with the aforementioned two opposite characteristics, namely improving the physical property of the polyethylene and preventing the formation of F.E. is impossible.

/3

#### Objective of the invention

The present inventor investigated a means for solving the aforementioned problems of the prior art and discovered that the aforementioned problem of F.E. formation could be solved by producing low molecular weight polymer in an initial stage (first stage) and high molecular weight polymer in a latter stage (second stage) while continuously moving the polymerization mixture and adding a glycol ether

compound continuously to said polymerization mixture in a production method of polyethylene by multi-stage polymerization, thus achieving the present invention.

As clearly shown in the aforementioned description, the objective of the present invention lies in providing a method with excellent productivity for producing polyethylene having excellent molding/processing property, physical properties and appearance as well as being suitable for hollow molding and extrusion molding.

#### Constitution/effect of the invention

The present invention consists of the following main constitution (1) and the implementing constitution of (2)-(5).

1. A method for producing polyethylene by continuous, multi-stage polymerization wherein a low molecular weight polymer is produced in a first stage of polymerization and a high molecular weight polymer is produced in a second stage of polymerization from ethylene with a Ziegler-type catalyst in the presence of a solvent and hydrogen using multiple polymerization reactors in series, and said method for producing polyethylene by continuous, multi-stage polymerization is characterized in that a glycol compound is added continuously to the polymerization mixture, which is extracted from said first polymerization stage before entering the second polymerization stage, at 0.1-10 mol/atom versus the transition metal atom carried by the catalyst in said mixture.

2. The method for continuous production of polyethylene described in previous item (1), wherein a small quantity of  $\alpha$ -olefin (excluding ethylene) is fed to the first stage and/or the second stage of polymerization for copolymerization with ethylene.

3. The method for continuous production of polyethylene described in previous item (1), wherein one tank or a series of 2 tanks and a catalytic system consisting of titanium-supporting solid catalytic substance (I) and an organic aluminum compound (II) are utilized in the first stage of polymerization.

4. The method for continuous production of polyethylene described in previous item (3), wherein the reaction product produced by reacting solid product (IV), obtained by reacting a trivalent metal halide with a divalent metal hydroxide, oxide, carbonate, complex salts thereof or divalent metal compound hydrate, with polysiloxane (V) and tetravalent titanium compound (VI) is utilized as the titanium-supporting solid catalytic substance (I).

5. The method for continuous production of polyethylene described in previous item (1) wherein,

(i) the first stage of polymerization is conducted in a saturated hydrocarbon solvent at a polymerization temperature of 50-120°C and polymerization pressure of 2-70 kg/cm<sup>2</sup> under the condition of having a gas phase at the upper reactor by feeding 30-80 wt% of the total quantity of ethylene and hydrogen to maintain an ethylene to hydrogen molar ratio of 1/3.0 to 1/7.0 in the gas phase in the polymerization reactor;

(ii) the second stage of polymerization is conducted by drawing the polymer suspended in the solvent to a pressure of 1-60 kg/cm<sup>2</sup> after completing the first stage of polymerization and recycling at least part of the hydrogen in the gas phase back to the first stage of polymerization, followed by polymerizing at polymerization temperature of 30-100°C and polymerization pressure of 2-70 kg/cm<sup>2</sup> under the condition of having a gas phase for said suspended polymer product by feeding 10-70 wt% of the total quantity of ethylene and hydrogen to maintain an ethylene to hydrogen molar ratio of 1/0.001 to 1/0.1 in the gas phase in the polymerization reactor.



In the production method of the present invention, the polymerization is first started by supplying the catalyst to the first stage of polymerization, and the first stage of polymerization is conducted at a polymerization temperature of 50-120°C, preferably 70-100°C, and polymerization pressure of 2-70 kg/cm<sup>2</sup>, preferably 5-50 kg/cm<sup>2</sup>, in the presence of a saturated hydrocarbon solvent and under the condition of having a gas phase in the upper reactor. The molecular weight of the polymer formed is regulated by feeding ethylene and hydrogen to maintain an ethylene to hydrogen molar ratio of 1/3.0 to 1/7.0 in the gas phase in the polymerization reactor. In this respect, the molecular weight of the polymer produced is  $1.5 \times 10^4$ - $6 \times 10^5$  in terms of weight-average molecular weight (Mw). The quantity of the polymer produced is regulated by supplying 30-90% of the total quantity of ethylene. /4

After completing the first stage of polymerization, the polymer product suspended in the solvent is drawn to an area with a pressure of 1-60 kg/cm<sup>2</sup> and dissolved in the solvent while at least part of the hydrogen in the first stage of polymerization is extracted from the polymerization system. The low pressure region in the aforementioned pressure area is in general set in the mid section of each stage and it can be furnished at either of the polymerization stages. The pressure drop of the first stage of the polymerization and the low pressure region is determined by the quantity of hydrogen required for the second stage of polymerization.

The polymer suspended in the solvent with most hydrogen extracted is then guided into the second stage of polymerization using a transporting means such as a transporting pump.

In the method of the present invention, a glycol ether (III) is added continuously, at a ratio to solid substance containing titanium (I), [(III)/titanium in (I)] = 0.1-10 (mol/atom), to the polymerization mixture before or after the aforementioned extraction of the gas phase. Also, glycol ether (III) may be added at the second stage of polymerization.

The second stage of polymerization is conducted by setting a new polymerization temperature of 30-100°C, preferably 40-90°C, and polymerization pressure at 2-70 kg/cm<sup>2</sup>, preferably 5-50 kg/cm<sup>2</sup>, and maintaining a gas phase in the upper part of the reactor for the polymerization system of the second stage. The molecular weight of the polymer formed is regulated by feeding ethylene and hydrogen to maintain an ethylene to hydrogen molar ratio of 1/0.001 to 1/0.1 in the gas phase in the polymerization reactor. In this respect, the molecular weight of the polymer produced is  $2 \times 10^{\text{[illegible]}}$ - $8 \times 10^{\text{[illegible]}}$  in terms of weight-average molecular weight (Mw). The quantity of polymer produced is regulated by supplying 10-70% of the total quantity of ethylene. In general, the molecular weight from the second stage depends on the hydrogen dissolved in the solvent, but new hydrogen may be supplied.

The molar ratio of ethylene to hydrogen for the first stage and the second stage of polymerization and quantity of ethylene supplied are determined by the usage of the final polymer product obtained.

The molar ratio of ethylene to hydrogen for the first stage of polymerization is 1:3.0-7.0 and the quantity of ethylene supplied is 30-90%, preferably 40-60%, of the total quantity of ethylene supplied. Additionally, the molar ratio of ethylene to hydrogen for the second stage of polymerization is 1:0.00-0.1 and the quantity of ethylene supplied is 30-90%, preferably 40-80%, of the total quantity of ethylene supplied.

Examples of the glycol ethers utilized in the present invention include ethylene glycol monoalkyl ether, ethylene glycol dialkyl ether, propylene glycol monoalkyl ether and propylene glycol dialkyl ether, and more specifically, ethylene glycol monomethyl ether, ethylene glycol dimethyl ether, ethylene glycol monoethyl ether, ethylene glycol diethyl ether, ethylene glycol monopropyl ether, ethylene glycol dipropyl ether, ethylene glycol monobutyl ether, ethylene glycol dibutyl ether, propylene glycol monomethyl ether, propylene glycol dimethyl ether, propylene glycol monoethyl ether, propylene glycol diethyl ether, propylene glycol monopropyl ether, propylene glycol dipropyl ether, propylene glycol

/5

monobutyl ether and propylene glycol dibutyl ether can be cited. Furthermore, glycol condensation products such as diethylene glycol monoalkyl ether, diethylene glycol dialkyl ether, triethylene glycol monoalkyl ether, triethylene glycol dialkyl ether, tetraethylene glycol monoalkyl ether, tetraethylene glycol dialkyl ether, dipropylene glycol monoalkyl ether, dipropylene glycol dialkyl ether, tripropylene glycol monoalkyl ether, tripropylene glycol dialkyl ether, tetrapropylene glycol monoalkyl ether, tetrapropylene glycol dialkyl ether, polyethylene glycol monoalkyl ether, polyethylene glycol dialkyl ether, polypropylene glycol monoalkyl ether and polypropylene glycol dialkyl ether can be cited, wherein the alkyl groups represent linear hydrocarbons of 1-20 carbons. Glycol ethers obtained by reacting ethylene oxide and propylene oxide can also be utilized. The quantity of these ethers (III) utilized varies with the types of glycol ethers owing to their different effects, but the mol/atom ratio of the ether to the transition metal in the catalytic substance (I) is: (III)/transition metal in (I) = 0.1-1.0. Specifically, said (III) is preferably incorporated to be 30-80% based on 100% for the catalytic substance without adding glycol ether.

The reason for the excellent effect of glycol ether preventing the formation of P.E. is not yet clear, but the present inventor offers the following hypothesis. That is, the catalyst is retained for a significantly shorter time compared to the normal average retention time before being transported from the first stage of polymerization to the second stage, wherein it is selectively deactivated by glycol ether and the polymerization is slowed, which in turn results in significant inhibition of the formation of particles of high polymer (cause of F.E.).

If the quantity added is too large, the deactivation of the short-path catalyst is too significant and the reduction of the overall catalytic activity is too great, making it very uneconomical, and that the control of the ratio of the degree of polymerization of polymerization process (i) to the degree of polymerization of polymerization process (ii) is restricted, which is not desirable. Contrarily, if the quantity of (III) is

too little, the selective deactivation of the aforementioned short-path catalyst is insufficient, which is not desirable either.

The reason that the glycol ethers (III) utilized in the present invention exhibit significantly better effects compared to other electron-donating compounds such as ketones, amines, amides, alkyl ethers, carboxylic esters and halogenated compounds is not entirely clear, but it is believed that said compounds (III) react with organic aluminum compounds (II) to form complexes insoluble in inert solvents that are unable to react with the catalyst residing inside the polymer particles but can significantly deactivate the short-path catalyst predominately. More specifically, the formation of a liquid complex insoluble in the inert solvent and incapable of penetrating into the polymer particles is considered a required property for the complex.

The catalyst for the method of production of the present invention is supplied to the first stage of polymerization stage.

Multiple reactors are in general arranged in series in the multi-stage polymerization of the present invention, but multiple reactors connected in parallel (or partly in parallel arrangement) can also be utilized in the first stage and/or the second stage of polymerization.

The solvents utilized in the polymerization of the production method of the present invention include saturated hydrocarbons of 4-15 carbons, and butane, pentane, hexane, heptane, octane and kerosene can be cited as the examples.

The catalyst utilized in the production method of the present invention is a Ziegler-Natta type catalyst, preferably a combination of solid catalytic substance (I) containing titanium with an organic aluminum compound. More specifically, solid product (I) can be produced by reacting solid product (IV), which is obtained from the reaction of a trivalent metal halide with a divalent metal hydroxide, oxide, carbonate, their complex salts or divalent metal compound hydrate, with polysiloxane (V) and a tetravalent

/6

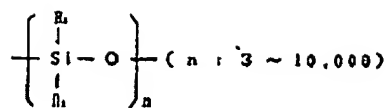
titanium compound. The solid product produced is then combined with organic aluminum compound (III).

Examples of the trivalent metal halides include aluminum trichloride (anhydrous) and iron trichloride (anhydrous).

Examples of the aforementioned divalent metal hydroxides (occasionally referred to as divalent metal compounds hereafter) include hydroxides such as  $\text{Mg}(\text{OH})_2$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{Zn}(\text{OH})_2$  and  $\text{Mn}(\text{OH})_2$ , examples of the oxides include  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{ZnO}$  and  $\text{MnO}$ , examples of complex oxides include  $\text{MgAl}_2\text{O}_4$ ,  $\text{Mg}_2\text{SiO}_4$  and  $\text{Mg}_5\text{MnO}_4$ , examples of the carbonates include  $\text{MgCO}_3$ ,  $\text{MnCO}_3$  and  $\text{CaCO}_3$ , examples of hydrates of halides include  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  and  $\text{KMgCl}_2 \cdot 6\text{H}_2\text{O}$ , an example of the hydrate of complex salt containing oxide and halide is  $8\text{MgO} \cdot \text{MgCl}_2 \cdot 15\text{H}_2\text{O}$ , an example of the hydrate of complex salt containing divalent metal oxides is  $3\text{MgO} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ , an example of the hydrate of complex salt of carbonate and hydroxide is  $3\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$  and an example of the hydrate of hydroxide-carbonate containing divalent metal is  $\text{Mg}_6\text{Al}_2(\text{OH})_6\text{CO}_3 \cdot 4\text{H}_2\text{O}$ .

Solid product (IV) is produced from the reaction of a trivalent metal halide with a divalent metal compound. Before carrying out this reaction, the mixture is preferably mixed thoroughly for 100 h with a ball mill, or mixed for 1-10 h with a vibration ball mill, followed by pulverizing. The mixing ratio of the trivalent metal halides and the divalent metal compounds is in general 0.1-20 in terms of atomic ratio of the divalent metal to the trivalent metal, and the ratio preferably in the range of 1-10. The reaction temperature is in general 20-500°C, preferably 50-300°C. The appropriate reaction time is 30 min-50 h, but if the reaction temperature is on the low side, the reaction is carried out for a longer period of time to insure no un-reacted residual trivalent metal.

Polysiloxanes (V) are linear or cyclic siloxane polymers represented by general formula



wherein R represents the same or different groups capable of bonding with the silicon atom, and examples of the compounds utilized in the present invention include those having one group or more than one group selected from hydrogen, hydrocarbon groups such as alkyl groups and aryl groups, halogens, alkoxy groups or arylalkoxy groups and aliphatic acid groups, which are bonded and distributed at various ratios in the molecule. The compounds generally utilized are those wherein the R in the aforementioned formula represents alkyl groups. The specific examples of alkylsiloxane polymers include lower polymers such as octamethyltrisiloxane  $\text{CH}_3(\text{Si}(\text{CH}_3)_2\text{O})_2\text{Si}(\text{CH}_3)_2$  and octaethylcyclotetrasiloxane  $[\text{Si}(\text{C}_2\text{H}_5)_2\text{O}]_4$ , and other alkylsiloxane polymers such as dimethylpolysiloxane  $[\text{Si}(\text{CH}_3)_2\text{O}]_n$ , ethylpolysiloxane  $[\text{SiH}(\text{C}_2\text{H}_5)\text{O}]_n$  and methylethylpolysiloxane  $[\text{Si}(\text{CH}_3)(\text{C}_2\text{H}_5)\text{O}]_n$ , and arylsiloxane polymers such as hexaphenylcyclotrisiloxane  $[\text{Si}(\text{C}_6\text{H}_5)_2\text{O}]_2$  and diphenylpolysiloxane  $[\text{Si}(\text{C}_6\text{H}_5)_2\text{O}]_n$ , and alkylaryl siloxane polymers such as diphenyloctamethyltetrasiloxane  $(\text{CH}_3)_3\text{SiO}[\text{Si}(\text{CH}_3)(\text{C}_6\text{H}_5)\text{O}]_2\text{Si}(\text{CH}_3)_3$  and methylphenylpolysiloxane  $[\text{Si}(\text{CH}_3)(\text{C}_6\text{H}_5)\text{O}]_n$ . Additional examples include alkyl hydrogen siloxane polymers and haloalkyl siloxane polymers and haloaryl siloxane polymers wherein  $R_1$  represents hydrogen or halogen and  $R_2$  represents hydrocarbon groups such as alkyl groups and aryl groups. Polysiloxanes wherein R represents alkoxy groups or aryloxy groups or aliphatic acid groups can also be utilized. Various mixtures of these polysiloxanes can also be utilized. The polysiloxanes utilized in the present invention are preferably in liquid form and the suitable viscosity is 10-10,000 cSt (25°C), preferably 10-1,000 cSt.

Examples of the tetravalent titanium compounds include titanium tetrachloride, titanium tetrabromide, tetraethoxytitanium, tetrabutoxytitanium, monochlorobutoxytitanium, dichlorodibutoxytitanium and trichloromonoethoxytitanium.

/7

The following examples show the specific methods for preparing solid product (I).

(1) Solid compound (IV), polysiloxane (V) and tetravalent titanium compound (VI) are mixed together and reacted simultaneously.

(2) Solid compound (IV) and polysiloxane (V) are mixed together, followed by adding tetravalent titanium compound (VI) and reacting.

(3) Solid compound (IV) and tetravalent titanium compound (VI) are mixed together, followed by adding polysiloxane (V) and reacting.

(4) Polysiloxane (V) and tetravalent titanium compound (VI) are mixed together, followed by adding solid compound (IV) and mixing and reacting.

All the aforementioned methods can be conducted in the presence or absence of a solvent.

The mixing ratio of solid compound (IV), polysiloxane (V) and tetravalent titanium compound (VI) are 10-10,000 g, preferably 20-5000 g, for polysiloxane (V) and 1-1,000 g, preferably 10-500 g, for tetravalent titanium compound (VI), versus 100 g of solid compound (IV), and 2-2,000 g, preferably 5-500 g, for tetravalent titanium compound (VI) versus 100 g of polysiloxane (V). The mixing is preferably carried out at -50°C to +30°C, but it is most generally carried out at room temperature (20°C). The mixing is preferably carried out by agitation. The reaction is carried out at 30-300°C, preferably 50-200°C for 10 min to 30 h while agitating after they are mixed thoroughly.

When mixing polysiloxane (V) and tetravalent titanium compound (VI) followed by mixing solid compound (I) to said mixture and reacting, the mixture of polysiloxane and tetravalent titanium compound (VI) is preferably allowed to stand at room temperature (about 20°C) to 100°C, more preferably under 60°C, for 1 min-5 h, before it is mixed with solid compound (IV).

After the reaction, the reaction product is filtered and washed repeatedly with a solvent by a conventional method, followed by removing the un-reacted titanium compound and polysiloxane and drying the product. Accordingly, solid compound (I) is obtained.

When conducting mixing and reaction to produce compound (I), the presence of a solvent is not absolutely necessary, but preferably any or all of the aforementioned ingredients are dissolved or dispersed in a solvent beforehand to facilitate better mixing. A quantity of less than about 10 times (by weight) of the total quantity of the aforementioned ingredients is quite sufficient for the solvent utilized. Examples of the solvents utilized in the preparation of solid compound (I) include aliphatic hydrocarbons such as hexane, heptane, octane, nonane and decane; aromatic hydrocarbons such as benzene, toluene, xylene, ethylbenzene and cumene; halogenated aromatic compounds such as chlorobenzene, dichlorobenzene and trichlorobenzene; and halogenated hydrocarbons such as carbon tetrachloride, chloroform, dichloroethane, trichloroethylene, tetrachloroethylene and carbon tetrabromide.

Examples of the organic aluminum compounds (II) include trialkylaluminums such as triethylaluminum, tri-isobutylaluminum and trihexylaluminum; dialkylaluminum monochlorides such as diethylaluminum monochloride; ethylaluminum sesquichloride and ethylaluminum dichloride. Alkoxyalkylaluminums such as monoethoxydiethylaluminum and diethoxymonoethylaluminum can also be utilized.

#### Effect of the invention

/8

As shown clearly in the aforementioned description, the present invention is effective in forming almost no F.E. even if the molecular weight is significantly broadened by multi-stage polymerization,



which makes it possible to produce polymers having extremely excellent appearance while also having improved physical properties and processing properties compared to conventional products.

#### Description by application examples

The MIs (melt index) of the application examples and the comparative examples were measured in accordance with ASTM-D1238(E). The Mw/Mn (Mw is the weight-average molecular weight and Mn is the number-average molecular weight) was determined by gel permeation chromatography.

The film utilized was a sample of thickness of 10  $\mu\text{m}$  produced with an inflation film molding machine (50 mm  $\phi$ , 75 rpm; manufactured by Blaco [transliteration] Company) at 180-200°C. The discharge quantity was observed for the melted resin during production. The punching impact strength of the film obtained was tested in accordance with ASTM-D78t and the haze value was tested in accordance with ASTM-D1003 and the fish eyes were evaluated by measuring the number of high polymer particles with diameters greater than 50  $\mu\text{m}$  in 1000-mL film.

#### Application Example 1

##### (1) Production of solid product (IV)

5.0 kg magnesium hydroxide and 12 kg aluminum trichloride (anhydrous) were mixed and pulverized at room temperature for 2 h in an 80-L vibration mill, and the content was transferred to a 30-L baking reactor and reacted wherein at 150°C for 5 h. Subsequently, the reaction product was chilled and subjected to micro-pulverization in the vibration mill to obtain 15 kg solid product (IV).

##### (2) Production of solid product (I)

20 L toluene, 10 kg linear dimethylpolysiloxane (viscosity 100 centistokes) and 8.0 kg titanium tetrachloride were added to a 100-L reactor equipped with an agitator and mixed at room temperature.

Subsequently, 10 kg solid product (IV) was added to the mixture and reaction was carried out at 80°C for 3 h. Afterward, the supernatant was removed, and 20 L toluene, 3 kg linear dimethylpolysiloxane (viscosity 100 cSt) and 3 kg tetra-n-butyl ortho-titanate were added to the residual solid product and reaction was carried out wherein at 80°C for 2 h. After the reaction, the reaction product was filtered with a filtering device and the solid product from the filtration was repeatedly washed with 80 L hexane and filtered until no un-reacted titanium compound or un-reacted polysiloxane was detected in the filtered solvent. The solid product after washing was dried under vacuum to obtain solid product (I). The content of titanium in the solid product (I) was 83 mg per gram.

The operations for the aforementioned reaction (1) and (2) were conducted in a nitrogen atmosphere containing no moisture.

### (3) Preparation of the catalyst

40 L n-hexane, 600 g triethylaluminum and 160 g of the aforementioned solid product (I) obtained were fed to a tank of inner volume of 50 L equipped with an agitator to prepare a catalyst slurry to be supplied to the polymerization reactor.

### (4) Polymerization method

Polymerization was carried out using the device shown in the figure below. 3kg/h ethylene, 30 L/h n-hexane and 150 mL/h of the aforementioned catalyst slurry were fed to the 150 L reactor (1), and hydrogen was supplied to maintain the hydrogen/ethylene concentration ratio of 4.5/1 (molar ratio) in the gas phase in the polymerization reactor by monitoring the analytical values on processing gas chromatography. The pressure for the polymerization at this point was 12 kg/cm<sup>2</sup>-G. Microadjustment was conducted for the quantity of catalyst slurry supplied to maintain the pressure for the polymerization at 12 kg/cm<sup>2</sup>-G. The reaction temperature was maintained at 90°C.

The slurry extracted from the polymerization reactor (1) was supplied to degassing tank (1). 214 mg/h diethylene glycol dimethyl ether was added to degassing tank (1) while adjusting the temperature to 70°C and the pressure to 0.5 kg/cm<sup>2</sup>-G. The slurry extracted from degassing tank (1) was supplied to polymerization reactor (2).

The temperature in polymerization reactor (2) was adjusted to 80°C and 3 kg/h ethylene was fed to it while hydrogen was supplied to maintain the hydrogen/ethylene concentration ratio at 0.08/1 (molar ratio) by monitoring the analytical values on processing gas chromatography. The polymerization pressure was 6 kg/cm<sup>2</sup>-G at this point.

The slurry leaving polymerization reactor (2) was subjected to pressure drop in degassing tank (2) before being sent to the after treatment process wherein the catalyst was deactivated with methanol, followed by separating, drying and recovering it as powder (the quantity of recovery was about 5.5 kg/h). During the process, slurry was sampled from degassing tank (1) and analysis was performed together with the powder product. The results are shown in the table below.

/9

#### (5) Granulating method

0.1% phenolic thermal stabilizer and 0.1% calcium stearate were added to the aforementioned powder product obtained and mixed wherein, followed by granulating with an extrusion granulating machine with screw diameter of 40 mm.

#### (6) Filming evaluation

10 μ tubing film was produced by air-cooling inflation from the aforementioned granulates produced by extruding from a ring die using an extruder with screw diameter of 50 mm and screw L/D = 25.

The film forming property and the appearance were both excellent and only 2 fish eyes were observed. The film punching impact strength was also excellent.

### Comparative Example 1

The same operation was conducted as in Application Example 1 except that feeding of diethylene glycol dimethyl ether to degassing tank (1) was omitted. Many fish eyes were observed and the appearance was poor while the punching impact strength was also reduced.

### Application Examples 2 and 3, Comparative Examples 2 and 3

The same operations were conducted as in Application Example 1 except that feeding of diethylene glycol dimethyl ether to degassing tank (1) was altered. In Comparative Example 2, the effect of preventing the formation of fish eyes was insufficient because the amount of the compound incorporated was too little; in Comparative Example 3, the catalyst was deactivated and the polymerization in polymerization reactor (2) was significantly reduced and no objective product was obtained because the amount of compound incorporated was too large.

### Application Examples 4-7

The same operations were conducted as in Application Example 1 except that feeding of diethylene glycol dimethyl ether to degassing tank (1) was changed to feeding diethylene glycol monobutyl ether, tetraethylene glycol dimethyl ether, diethylene glycol diethyl ether and diethylene glycol dipropyl ether for Application Examples 4-7, respectively, at the molar ratios shown in the table below. Films having excellent appearance and excellent punching impact strength were obtained.

### Comparative Examples 4-7

The same operations as in Application Example 1 were conducted except that acetophenone, methyl para-toluate, triethylamine and dimethyl ether were utilized respectively to replace diethylene glycol

dimethyl ether. Almost no effect of preventing the formation of fish eyes was observed for these electron-donating compounds.

#### Application Example 8

The same operation was conducted as in Application Example 1 except that the H<sub>2</sub>/C[illegible] molar ratio in the gas phase of polymerization reactors (1) and (2) was altered.

#### Comparative Example 8

The same operation as in Application Example 8 was conducted except that feeding of diethylene glycol dimethyl ether was omitted. Many fish eyes were observed and the appearance was poor while the punching impact strength was also reduced.

#### Application Example 9

The same operation was conducted as in Application Example 1 except that the H<sub>2</sub>/C[illegible] molar ratio in the gas phase of polymerization reactors (1) and (2) was altered.

#### Comparative Example 9

The same operation as in Application Example 9 was conducted except that feeding of diethylene glycol dimethyl ether was omitted. Reducing the Mw/Mn resulted in a tendency of reducing the number of FE but the effect was insufficient.

### Comparative Example 10

The H<sub>2</sub>/C[illegible] concentration ratios in polymerization reactors (1) and (2) in Application Example 1 were changed and the Mw/Mn was increased. Many FE were observed and the film forming stability was poor.

### Comparative Example 11

The H<sub>2</sub>/C[illegible] concentration ratios in polymerization reactors (1) and (2) in Application Example 1 were changed and the Mw/Mn was decreased. The FE condition was excellent, but the fluidity during film forming was poor and the film thickness was uneven, and stable film could not be produced.

/10

Table

	① 実施例 1	② 比較例 ①	① 実施例 2	③ →	② 比較例 ②	④ →
重合器(1)						
H <sub>2</sub> /C <sub>3</sub> モル比	4.5 / 1.0	→	→	→	→	→
脱ガス槽(1)						
MI g/10分	480	500	480	490	500	500
GE	A	—	A	→	→	→
GE/触媒中のTi モル比	2.0	—	0.5	5.0	0.05	5.0
重合器(2)						
H <sub>2</sub> /C <sub>3</sub> モル比	0.06 / 1.0	→	→	→	→	→
製品パウダー						
MI g/10分	0.05	0.05	0.04	0.06	0.05	5.0
FE/所	25	25	26	24	25	12
フィルム						
FE ヶ/1000cm <sup>2</sup>	2	55	5	0	45	—
外 観	良 ④	⑤ 不良	良 ④	良 ④	⑤ 不良	—
製膜性	良	良 ④	良 ④	良 ④	良 ④	—
打抜耐擦強度 kg/cm <sup>2</sup>	210	85	180	200	110	—

A : ジエチレングリコールジメチルエーテル

⑥ 炭のつづき

	①				②			
	実施例 4	5	6	7	比較例 ⑧	⑨	⑩	⑪
重合器(1)								
H <sub>2</sub> /C <sub>3</sub> モル比	→	→	→	→	4.5/1.0	→	→	→
脱ガス槽(1)								
MI g/10分	510	490	490	500	490	520	490	510
GE	B	C	D	E	F	G	H	I
GE/触媒中のTi モル比	3.0	1.5	2.0	2.0	2.0	2.0	2.0	4.0
重合器(2)								
H <sub>2</sub> /C <sub>3</sub> モル比	→	→	→	→	0.06/1.0	→	→	→
製品パウダー								
MI g/10分	0.04	0.05	0.04	0.04	0.04	0.05	0.05	0.04
PC/PC	25	24	24	25	25	24	24	25
フィルム								
FE	3	1	4	2	50	65	55	45
η/1000cm <sup>2</sup>								
外観	良	良	良	良	不良	不良	不良	不良
製膜性	良	良	良	良	良	良	良	良
打抜き強度 kg/cm <sup>2</sup>	190	200	180	190	110	75	95	120

B: ジエチレングリコールモノブチルエーテル, C: テトラエチレングリコールジメチルエーテル  
D: ジエチレングリコールジエチルエーテル, E: ジエチレングリコールジプロピルエーテル  
F: アセトフェノン, G: メチルパラトルエート, H: トリエチルアミン, I: ジメチルエーテル

⑥ 炭のつづき

	①		②		③	
	実施例 8	比較例 ⑫	実施例 9	比較例 ⑬	⑭	⑮
重合器(1)						
H <sub>2</sub> /C <sub>3</sub> モル比	6.0/1.0	→	3.5/1.0	→	9/1.0	2.0/1.0
脱ガス槽(1)						
MI g/10分	1050	1040	210	215	2800	50
GE	A	→	A	→	A	→
GE/触媒中のTi モル比	2.0	→	2.0	→	2.0	→
重合器(2)						
H <sub>2</sub> /C <sub>3</sub> モル比	0.045/1.0	→	0.08/1.0	→	0.009/1.0	0.2/1.0
製品パウダー						
MI g/10分	0.03	0.03	0.05	0.05	0.03	0.07
PC/PC	29	29	19	20	34	15
フィルム						
FE	6	110	0	35	35	0
η/1000cm <sup>2</sup>						
外観	④ 良	⑤ 不良	④ 良	不良	不良	不良
製膜性	良	不良	良	不良	不良	不良
打抜き強度 kg/cm <sup>2</sup>	240	120	185	75	55	→

A: ジエチレングリコールジメチルエーテル

- Key 1 Application example
- 2 Comparative example
- 3 Polymerization reactor (1)
- H<sub>2</sub>/C[illegible] molar ratio

Degassing tank (1)

MI g/10 minute GE

Molar ratio of GE/Ti in catalyst

Polymerization reactor (2)

H<sub>2</sub>/C[illegible] molar ratio

Powder product

MI g/10 minute GE

Film FE

Number/1000 cm<sup>3</sup>

Appearance

Film forming property

Puncture/impact strength kgcm/n

4 Good

5 Poor

6 Table (continued)

A: Diethylene glycol dimethyl ether

B: Diethylene glycol monobutyl ether

C: Tetraethylene glycol dimethyl ether

D: Diethylene glycol diethyl ether

E: Diethylene glycol dipropyl ether

F: Acetophenone

G: Methyl para-toluate

H: Triethylamine



I: Dimethyl ether

# Description of the figures

/12

Figure 1 shows the flowchart of the polymerization device utilized in the application examples of the present invention. Figure 2 is a descriptive diagram of the process of the production method of the present invention.

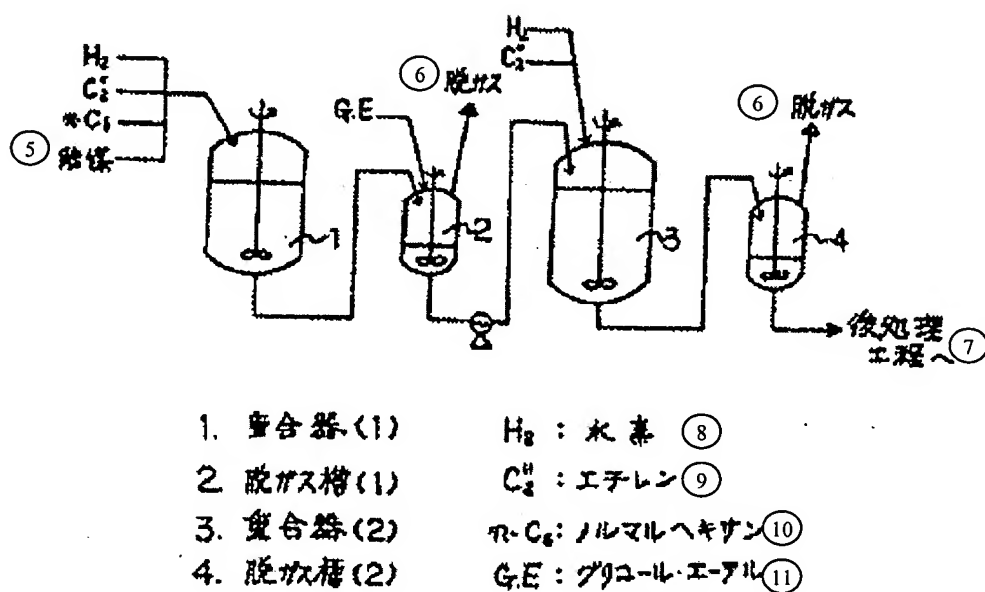


Figure 1

Key	1	Polymerization reactor (1)
	2	Degassing tank (1)
	3	Polymerization reactor (2)
	4	Degassing tank (2)
	5	Catalyst
	6	Degassing

- 7 To post-treatment process
- 8 Hydrogen
- 9 Ethylene
- 10 Normal hexane
- 11 Glycol ether

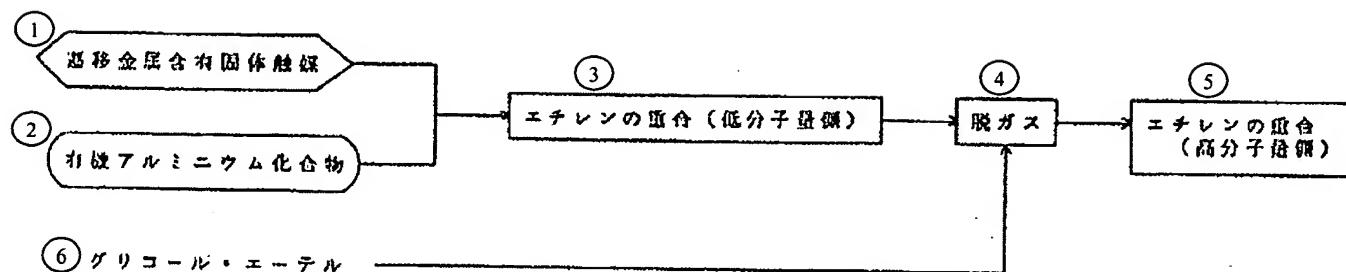


Figure 2

- Key
- 1 Solid catalyst containing transition metal
  - 2 Organic aluminum compound
  - 3 Polymerization of ethylene (low molecular weight)
  - 4 Degassing
  - 5 Polymerization of ethylene (high molecular weight)
  - 6 Glycol ether